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Dear Examiner Paden:

As you requested, enclosed is the document entitled "Developments in Dry Fractionation of Fats" which is referred to in the Amendment received by the PTO on May 27, 2003.

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DEVELOPMENTS IN DRY FRACTIONATION OF FATS

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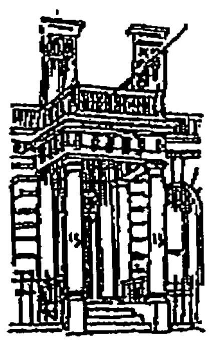

DEVELOPMENTS IN DRY FRACTIONATION

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The replacement of the fractional crystallization process from a solvent by a fractionation process from the melt is very attractive for several reasons. However, the solid-liquid separation when crystallizing from the melt is relatively poor compared with solvent fractionation. Significant improvements can be achieved by using membrane filter presses and multi-stage counter-current fractionation.

INTRODUCTION

The melting behaviour of oils and fats in foods is of great importance especially when these substances form the main component. Oils and fats consist of triacylglycerols (TAGs) and minor components like diacylglycerols, monoacylglycerols, vitamin A, D, E and phospholipids. The length of the acyl groups varies from 4 to 22 carbon atoms. The number of unsaturated bonds per acyl group varies in most of the vegetable fats from 0 to 3 in which the double bond may be in the cis or the trans configuration. Because of different requirements for different applications, variations in melting trajects per oil, per country and per season it is essential to modify the melting behaviour. In the oils and fats industry there are at least four important modification techniques: mixing, hydrogenation, interesterification and crystallization fractionation. Of these modification techniques mixing and fractionation are physical processes. Modification of fats with physical techniques is of strategic importance because in that way 'natural' foods are prepared.

FRACTIONATION PROCESSES

Generally the crystallization of fats takes place in suspension. Three fractionation processes can be distinguished:

- fractionation from a solvent (wet fractionation). The fat is dissolved in an organic solvent and partially crystallized by decreasing the temperature. The solid-liquid separation is usually carried out by using filtration (drum and belt filters). Generally the filter cake is washed with solvent. The boiling-points of solvent and fat differ so much that the solvent can subsequently be removed quantatively by distillation.
- Fractionation with detergents (Lanza fractionation). Crystallization takes place from the melt and the crystals migrate to the water phase because of the superior wetting properties of this phase. The phases are separated in centrifuges.
- Fractionation from the melt (dry fractionation).

One of the criteria for a successful operation is the separation efficiency (SE) which is defined as the friction solid phase in the filter cake (stearin). Fractionation from solvent gives the highest SE (0.85-0.95). The SEs obtained via dry and detergent fractionation are more or less the same and are significantly lower than those of solvent fractionation. A second advantage besides the good SE in the solvent fractionation process is the fact that large quantities of crystals can be removed in one stage. The disadvantages of the process are the high process costs and the use of chemicals. With the current trends 'natural' and 'green' (as well as cost reduction) dry fractionation as a modification tool is becoming of greater importance.

DRY FRACTIONATION

When shifting from solvent to dry fractionation the following problems can be expected:

- less selective crystallization
- removal of less crystals per fractionation stage
- poorer solid-liquid separation between liquid and crystals.

Up to the beginning of the eighties the solid-liquid separation in dry fractionation was performed by filtration using drum and belt filters in conformity with the solvent fractionation process. The filter cake in dry fractionation contained around 35 % solid phase compared with 90 % in solvent fractionation after filtration and washing (depending on the type of fat). The low percentage of solid phase in the filter cake at the end of filtration in dry fractionation can be explained as follows:

- during crystallization the crystals agglomerate resulting in a system of agglomerates with olein (liquid) included and also olein between the agglomerates;
- the olein in the agglomerates (which may be up to 50 % of the volume of the agglomerate') will not be removed during filtration because the flow resistance in the agglomerates is much higher than on the outside
- after settling of the crystals by filtration air throughput generally occurs through some larger channels and the pressure difference over the filter cake will disappear. The porosity of a bed with randomly packed spheres is approximately 40 %. After filtration the filter cake consists of up to 60 % of agglomerates which contain around 50 % olein. This indicates a solid phase content of 30 %.

In solvent fractionation the olein can be washed from between the agglomerates. The olein in the agglomerates is about 12 % at an oil/solvent ratio of 1:5 and a solid phase content of 30 % (with regard to the fat). This leads to an expected SE of about 90 % at an agglomerate porosity of 50 %.

PRESSING STAGE

Introduction of the membrane filter press increased the solid phase content from 35 % to around 50 % after filtration and pressing (depending on the type of oil). Despite the fact that the expression of filter cakes from oil slurries has become a common unit operation, theoretical knowledge on the expression of compressible filter cakes is still very limited. The most widely used models are those of Shirato[1,3] (combined Terzaghi-Voight model) and Vorobjov[4]

The models describe a consolidation process which is assumed to be a combination of primary and secondary consolidation. In the primary consolidation stage the particles rearrange to close packing (described by the Terzaghi model). The secondary consolidation stage involves particle deformation (described with the Voight model). In the models it is assumed that (i) the filter cake consists of solid particles which is not the case (the particles are porous and compressible); (ii) the filter cake is homogeneous on pressing which is also not in agreement with practice either and (iii) the creep deformation in the Voight model is negligible in comparison with the rate of liquid transport which does not apply for fats. The most significant disadvantage is that the model does not fit the experiments.

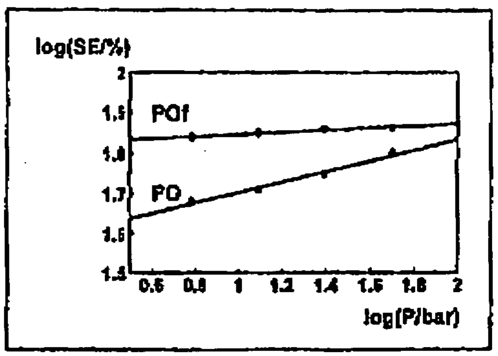
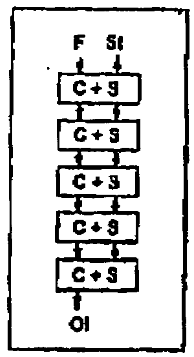


Figure 1:
SE-dependence on pressure for PO and POf slurries

A second complication in modelling is the fact that filtration and pressing kinetics differ according to the type of slurry. It was found that in a number of cases increased pressure can improve the solid-liquid separation. (however, only to a certain extent). For example, in the case of palm oil (PO) increasing the pressure (up to about 20 bar) will improve the SE. Slurries of palm olein (POf) however have a high SE after filtration and show hardly any dependence on pressure (Fig. 1).

MULTI-STAGE COUNTER-CURRENT FRACTIONATION

Multi-stage counter-current processing only became meaningful after the introduction of the membrane filter press. The problem that in dry fractionation not enough solid phase content can be removed in one step at a sufficiently high SE can be solved by diluting the feed with olein from the previous stage.



In Figure 2 a possible process scheme for multi-stage counter-current fractionation is given. In the scheme every block represents a batchwise crystallization and solid-liquid separation. The olein of each block moves to the block below and the stearin to the block above. In principle a lot of combinations are possible. Counter-current fractionation has advantages over multi-step fractionation (in which also fractions are refractionated but without using the by-products as diluent to the feed of the next stage) with view to composition, yield and the number of byproducts.

Figure 2:
Process scheme of multi-stage counter-current fractionation (C+S = crystallization+ separation)

In Fig. 3 a hypothetical and very simple phase diagram is given. This diagram can be used to show the effect of counter-current fractionation.

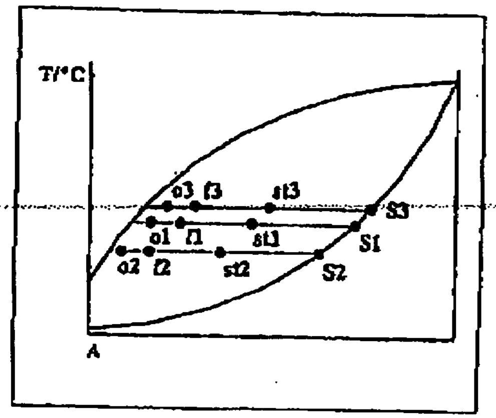


Figure 3: Hypothetical phase diagram: the first three fractionations of a counter-current process.

We start for example with a feed with composition f1, that is dry fractionated to give an olein (o1) and a stearin (st1) phase, containing 50 % solids (s1). (Note: the olein is not on the equilibrium curve!). The olein of the first stage is refractionated in the second stage (o1=f2). In the second stage again an olein (o2) and a stearin (st2) are obtained. The stearin from this stage (st2) is fed to the previous stage and mixed with f1. Therefore a new feed, f3 is formed. The stearin from this feed, st3, is enriched in component A compared with st1 (obtained without mixing with st2).

The diagram of Figure 3 cannot be used as such, because: (i) oil is not a binary system, (ii) it cannot be expected that during crystallisation an equilibrium is reached between solid and liquid phase and (iii) there is no complete solid solution. TAGs form mixed crystals or crystals with partial demixing. Also eutectics and peritectics might occur. However, the system on which the phase diagram is based; partition coefficients of components over both phases, is very useful.

The disadvantage of the counter-current process is that the experimental determination of the process conditions is very time-consuming whilst at least three cycles are needed to obtain steady state. For complicated schemes with partial olein reflux far more cycles are needed. In the partition coefficients or K-values model it is assumed, that the composition of the phases can be described by non-equilibrium phase diagrams or non-equilibrium partition coefficients. In a pragmatic approach classes of triacylglycerols (TAGs) are used instead of separate TAGs (SSS, SOS, SSO, SSL, SOO, rest). The partition coefficient is defined as the fraction of the component in the solid phase divided by the fraction of that component in the liquid phase. The coefficients are estimated by performing fractionation experiments and analysing feed and fractions. In a computer programme a lot of fractionation steps can be combined.

Figure 4: Two-stage counter-current fractionation compared to a two-step process with the same olein composition (B) and stearin yield (C) respectively. The numbers refer to SSS/SSO concentrations.

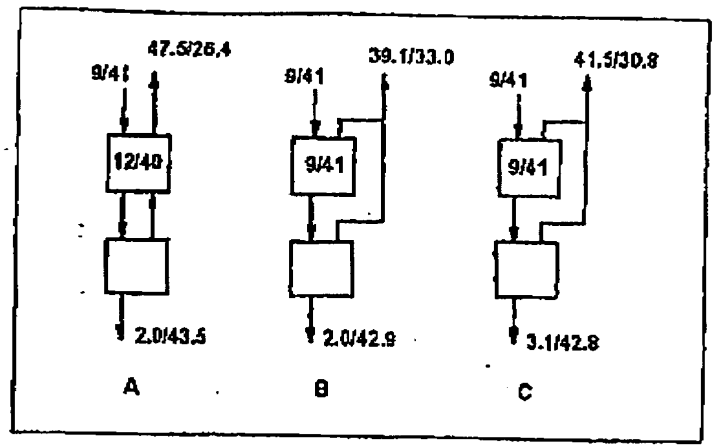


Figure 4 shows what can be achieved with double-stage counter-current fractionation. The fractionation of palm oil is compared with a double-stage fractionation (see process scheme). Scheme B represents a double-stage fractionation in which so much SPC is removed that the SSS content in the olein is comparable to that of scheme A. The difference shows in the composition of the stearin. With the counter-current process a SSS/SSO ratio of 47.5/26.4 % is achieved against 39.1/33.0 % in the double-stage process. In this case the olein yield for both processes differs. In scheme C so much SPC is removed that the stearin yield is the same as that of the counter-current fractionation process. In that case the SSS/SSO content of the stearin is 41.5/30.8. In both cases (B and C) the solid-liquid separation with the counter-current process is significantly better. It can be calculated that the same stearin composition could have been obtained with the double-stage process if in that process a SE of 63 % instead of 50 % was achieved. Therefore the counter-current process means an improvement of the overall separation efficiency.

CONCLUDING REMARKS

The solid-liquid separation in the dry fractionation process can be improved for certain types of slurries to some extent by optimizing the solid-liquid separation stage, but a better separation efficiency can also be obtained by applying multi-stage counter-current fractionation. Apart from optimized solid-liquid separation with counter-current processing the crystallization stage might offer possibilities for further improvement of the separation.

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